Comment on "Theory of nonlinear ac responses of inhomogeneous two-component composite films" [Phys. Lett. A 357, 475 (2006)].

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Abstract

In this comment, I point out to several mathematical mistakes in the above-referenced letter.

In a recent letter (1), Xu, Huang and Yu (referred to as XHY below) have derived effective nonlinear susceptibilities of graded composite films. The theoretical approach used by XHY is based on the perturbative theory developed previously in Ref. (2) by Yu (the same author as in the letter which is subject of this comment), Hui and Stroud. However, XHY make several mathematical mistakes in applying the formalism of Ref. (2), which are briefly detailed below.

XHY have considered a two-component film whose composition is varied in one dimension. More specifically, the volume fractions of the two components making up the film, p_1 and p_2 ($p_1 + p_2 = 1$) were assumed to depend on the linear coordinate $z \in [0, L]$. Nevertheless, the computation of effective nonlinear responses, given in Eqs. 1-15 of Ref. (1), was carried out for fixed values of p_1 and p_2. The dependence of effective linear and non-linear susceptibilities on z was then expressed through the dependence of p_1 and p_2 on z, as is evident from Eqs. 16,17 of Ref. (1). Thus, the gradation of the films was assumed to be slow enough, so that the effective susceptibilities could be physically defined as functions of z. This assumption can be reasonable and is not subject of this comment. However, the method used for the derivation of the effective constants *at fixed values of* p_1 *and* p_2 outlined in Eqs. 1-15 of Ref. (1) is erroneous.

The derivation mentioned above is based on Eq. 14 of Ref. (2). This equation gives a formula for computing the effective linear dielectric constant of a

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composite, ϵ_e, and, written in terms of the volume fractions p_1 and p_2 and the linear dielectric constants ϵ_1 and ϵ_2 of the components, has the form

$$\epsilon_e = p_1\epsilon_1\frac{\langle E_1^2\rangle}{E_0^2} + p_2\epsilon_2\frac{\langle E_2^2\rangle}{E_0^2} \ . \tag{1}$$

In this formula, $\langle E_1^2\rangle$ and $\langle E_2^2\rangle$ are the averages of the square of the (real-valued) linear electric field, computed inside the first and the second constituent of the film, respectively, and E_0 is the external electric field. Because E_1 and E_2 are *linear* fields, the ratios $\langle E_{1,2}^2\rangle/E_0^2$ are independent of E_0. Thus, Eq. 1 gives the effective linear dielectric constant of the composite in terms of the linear dielectric constants of its constituents as a weighted average. Incidentally, this definition of ϵ_e was obtained by equating the total electrostatic energy of a homogeneous sample occupying some volume V and characterized by the linear dielectric constant ϵ_e and that of a composite occupying the same volume and characterized by the constants $p_{1,2}$ and $\epsilon_{1,2}$. Of course, the ratios $\langle E_{1,2}^2\rangle/E_0^2$ must be computed by solving the electrostatic boundary value problem for each specific geometry of the composite.

In what follows, I detail three mistakes XHY have made in applying Eq. 1 to the the problem of computing the nonlinear responses of composite films.

The First Mistake At the onset, XHY use Eq. 1 to compute the averages $\langle E_1^2\rangle$ and $\langle E_2^2\rangle$, assuming that ϵ_e is given by some known function, $\epsilon_e = F(\epsilon_1, \epsilon_2, p_1, p_2)$. Namely, they write (Eqs. 2,3,7 of Ref. (1)):

$$\langle E_1^2\rangle = \frac{1}{p_1}\frac{\partial F(\epsilon_1, \epsilon_2, p_1, p_2)}{\partial \epsilon_1}E_0^2 \tag{2}$$

and analogously for $\langle E_2^2\rangle$. In writing this equation, XHY have ignored the fact that the averages $\langle E_1^2\rangle$ and $\langle E_2^2\rangle$ are themselves functions of both ϵ_1 and ϵ_2. Differentiation of Eq. 1 with respect to ϵ_1 (taking into account $\epsilon_e = F$) would yield

$$p_1\left(\langle E_1^2\rangle + \epsilon_1\frac{\partial\langle E_1^2\rangle}{\partial\epsilon_1}\right) + p_2\epsilon_2\frac{\partial\langle E_2^2\rangle}{\partial\epsilon_1} = \frac{\partial F(\epsilon_1, \epsilon_2, p_1, p_2)}{\partial\epsilon_1}E_0^2 \ . \tag{3}$$

Eq. 2 is derivable from Eq. 3 only if $\partial\langle E_1^2\rangle/\partial\epsilon_1 = \partial\langle E_2^2\rangle/\partial\epsilon_1 = 0$, which, obviously, is not the case.

The Second Mistake Application of Eq. 2 requires the knowledge of the function $F(\epsilon_1, \epsilon_2, p_1, p_2)$. To this end, XHY define F for the graded film as

a whole (not locally) by writing $F = L[\int_0^L \epsilon_{\rm MG}^{-1}(z)dz]^{-1}$ (Eq. 21 of Ref. (1)), where $\epsilon_{\rm MG}$ is the Maxwell-Garnett effective dielectric constant that can be found analytically from Eqs. 16,17 of Ref. (1). The first step in this procedure has not been justified in Ref. (1) and appears to be arbitrary. More importantly, the second step requires that the Maxwell-Garnett formula give the same result for the dielectric constant as Eq. 1 with properly computed field averages. But the two equations are, generally, not equivalent. In Ref. (2), a Maxwell-Garnett-type formula was derived from Eq. 1 for the case of spherical inclusions of volume fraction p_1 in the limit $p_1 \to 0$. But for mixing ratios close to 0.5, and for high-quality metal inclusions in a dielectric host with the electromagnetic frequency being close to the Frohlich resonance of a single inclusion (all of which is the case in numerical examples shown in Ref. (1)), the Maxwell-Garnett formula is known to be very inaccurate (3). In fact, it has been demonstrated in Ref. (3) that the Maxwell-Garnett theory provides a reasonable approximation only for $p_1 < 10^{-3}$.

Physically, computing the averages $\langle E_1^2 \rangle$ and $\langle E_2^2 \rangle$ by means of Eq. 2 (which is, also incorrect due to the First Mistake), where the analytical form of F is derived from the Maxwell-Garnett formula ignores the well-known phenomenon of strong fluctuations of electric field in resonant composites (4; 5).

The Third Mistake XHY make the most serious mistake when they state that the *nonlinear* susceptibilities can be obtained from Eq. 1 by viewing the constants $\epsilon_{1,2}$ as intensity-dependent, i.e., by making the substitutions $\epsilon_{1,2} \to \epsilon_{1,2} + \chi_{1,2}\langle E_{1,2}^2 \rangle$ in the arguments of the function F, and by expanding F with respect to the small parameters $\chi_{1,2}$. This procedure is mathematically expressed in Eq. 6 of Ref. (1) and is clearly erroneous. By definition, $\epsilon_{1,2}$ in Eq. 1 are the *linear* dielectric constants of the composite constituents, as well as ϵ_e is, by definition, the linear effective dielectric constant of the composite. Computation of higher-order effective susceptibilities would require computing higher moments of the field. For example, the formula derived in Ref. (2) for the effective third-order susceptibility is

$$\chi_e = p_1\chi_1 \frac{\langle E_1^4 \rangle}{E_0^4} + p_2\chi_2 \frac{\langle E_2^4 \rangle}{E_0^4} \ . \tag{4}$$

Thus, Eq. 6 of Ref. (1) is based on an incorrect interpretation of the theoretical results of Ref. (2)

Finally, the conclusion of Ref. (1) that "the harmonics [generated in a graded composite film] are significantly dependent on the gradation profiles as well as the width of the composite film" is technically (and trivially) correct. However, equations derived in Ref. (1) can not be used to "monitor the gradation profile as well as the width of the composite graded film by measuring the nonlinear

ac responses of the film subjected to an ac electric field" due to the errors described in this comment.

References

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